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### **Characterization of Nanoparticle Films and Structures Produced by Hypersonic Plasma Particle Deposition**

Christopher R. Perrey, Ryan Thompson, C. Barry Carter\*, Ashok Gidwani<sup>1</sup>, Rajesh Mukherjee<sup>1</sup>, Thierry Renault<sup>1</sup>, P. H. McMurry<sup>1</sup>, J. V. R. Heberlein<sup>1</sup>, and S. L. Girshick<sup>1</sup>

Department of Chemical Engineering and Materials Science

University of Minnesota, 421 Washington Ave. S.E., Minneapolis, MN 55455

<sup>1</sup> Department of Mechanical Engineering

University of Minnesota, 111 Church Street S.E., Minneapolis, MN 55455

\*corresponding author: carter@cems.umn.edu

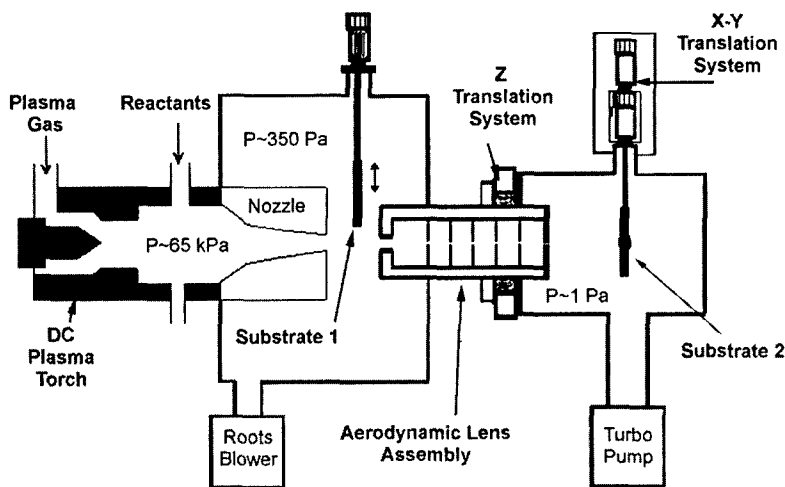
#### **ABSTRACT**

There is great potential for the use of nanostructures in numerous applications. Investigation of nanoparticle films and structures is an important area of research for the production of nanoengineered devices. However, for these devices to become a reality, a production method that can yield high-rate synthesis of nanostructured powders is necessary. The hypersonic plasma particle deposition (HPPD) process has been shown to be capable of such high-rate production of nanoparticle films and structures. Versatile in its ability to manufacture nanoparticles of different chemistries HPPD also has the capability of in situ particle consolidation and assembly. In this study, chemically diverse films and structures have been produced by HPPD on a variety of substrates. Using novel specimen preparation techniques, these nanoparticles have been characterized by TEM. Fundamental issues of importance have been investigated for both the nanoparticle structure and the constituent nanoparticles. These issues include nanoparticle crystallinity and defect structure. The chemical homogeneity and structural characteristics of the deposition are also investigated. This application of microscopy to aid process development has resulted in insights into the nanoparticle formation process and the dynamics of the HPPD process.

#### **INTRODUCTION**

There is currently great interest in the synthesis and processing of nanostructured materials, which are materials with grain sizes less than about 100nm. Such materials are often found to have properties superior to those of conventional bulk materials. Examples of enhanced properties include greater strength, hardness, reactivity, etc. Past developments in production and determination of the properties of these materials have been summarized in extensive reviews [1, 2]. The potential applications of these materials include wear resistant coatings, microparts for MEMS, ductile ceramics, new electronic and optical devices, and catalysts.

This work demonstrates the ability of hypersonic plasma particle deposition (HPPD) to produce deposits of nanostructured materials. Characterization of these deposits has led to a greater understanding of nanoparticle formation and the dynamics of the HPPD process.



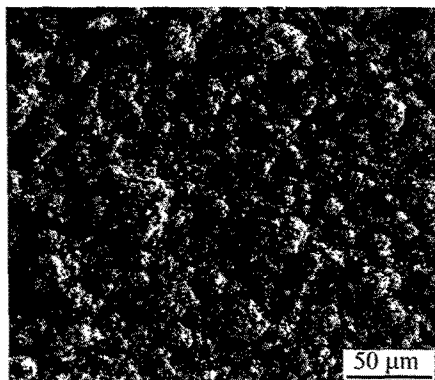
**Figure 1:** Schematic of the HPPD apparatus

## EXPERIMENTAL DETAILS

Hypersonic Plasma Particle Deposition (HPPD) involves a one-step process in which nanoparticles are both synthesized and deposited. The experimental set-up is shown schematically in Figure 1. The details of the experimental apparatus and operating conditions have been described previously [3, 4] and are briefly explained here. A 10 kW DC plasma torch operates with typical plasma forming gas feed rates of 30-37.5 slm of argon and 2-7.5 slm of hydrogen. The arc current varies between 200-275 A. The gas phase reactants are injected downstream of the plasma torch, where the temperatures are sufficiently high ( $> 4000\text{K}$ ) to dissociate the precursor vapors into their atomic form. The resulting gas mixture is then quenched through a converging boron nitride nozzle, leading to super saturation of vapors and subsequent nucleation of particles. The particle-laden gas is then accelerated by a free expansion into the vacuum chamber (maintained at about 2 Torr). The particles impact a substrate in one of the following two ways to form a deposit.

In the first process, called “continuous film deposition”, a molybdenum substrate is positioned normal to the flow, and particles as small as a few nanometers in diameter impact the substrate at high velocity to form a dense, nanostructured coating as seen in Figure 2. For example, a 20 nm particle is predicted by numerical calculations to impact the substrate with a velocity of about 1700 m/s. The typical growth rates for these films are 5-7  $\mu\text{m}/\text{min}$ .

In “focused beam deposition”, the second process, the molybdenum substrate is replaced by an aerodynamic lens assembly, which “focuses” [5] the particles to a narrow beam, with beam widths of the order of a few tens of microns. A second-stage substrate is placed downstream of the exit nozzle of the lens assembly. If this substrate is held stationary the nanoparticle beam



**Figure 2:** SEM image of the surface of a Ti-Si-N nanoparticle film deposited at 700 °C. The complex structure of the film is evident even at low magnifications.



**Figure 3:** A SiC nanoparticle tower, approximately 2 mm tall with a 40 μm half-height width, deposited with focused particle beam on a stationary substrate in 4 minutes. This implies a growth rate of approximately 8 μm/min for this structure.

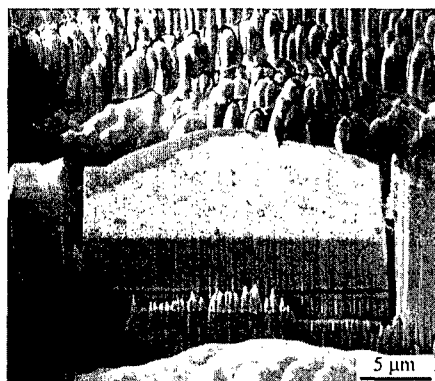
forms a high-aspect-ratio “tower” (Fig. 3). By translating the substrate one can use the particle beam to deposit lines and patterns. It is possible to deposit on a variety of substrates in this stage. So far, Si wafers,  $\text{Al}_2\text{O}_3$  wafers, and TEM support films have been used.

The HPPD process has deposited nanostructured films composed of elements from among the following: Si, Ti, C, and N. The reactants for pure Si and Ti deposits are  $\text{SiCl}_4$  and  $\text{TiCl}_4$ , respectively, while  $\text{CH}_4$  is injected to produce carbides and  $\text{N}_2$  (in the plasma) or  $\text{NH}_3$  (in the reaction zone) to produce nitride deposits. Average particle sizes for the HPPD process are in the range 10–30 nm.

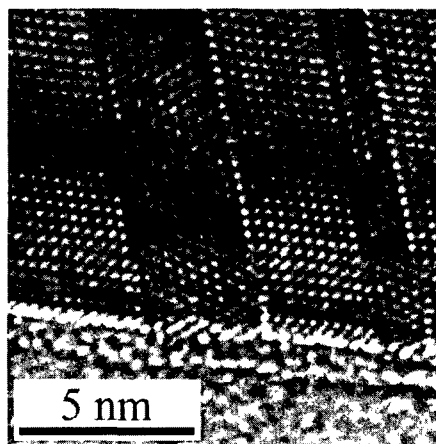
Nanoparticle films were prepared for TEM analysis using a FEI DB 235 focused ion beam (FIB) tool. Both the lift-out and self-supporting techniques for the FIB were employed [6–9]. Conventional TEM characterization was carried out using a Philips CM30. Analytical TEM and high-resolution TEM (HRTEM) were performed using a Philips CM200 and a spherical aberration-corrected Philips CM20, respectively.

## DISCUSSION

The surface of a Ti-Si-N nanoparticle film produced by HPPD (utilizing the “continuous film deposition” process) is shown in Figure 2. At low magnification, the film appears relatively uniform; however, at higher magnifications, the nanostructure of the film becomes evident. In order to characterize the sub-surface features of the films by TEM, special preparation techniques have been developed. The use of TEM is necessary for nanoscale characterization due to the versatility and resolution of the characterization techniques [10, 11]. However, the TEM specimens are required to be less than 3 mm in diameter and thin, with the final thickness dependent on the analysis desired [11]. For this study, the FIB was used to produce electron-transparent cross section specimens of the films: Figure 4 is a SEM image of a completed lift-out specimen of a  $\beta$ -SiC nanoparticle line produced with the focused beam deposition stage. It is



**Figure 4:** SEM image of a  $\beta$ -SiC nanoparticle structure prepared by the FIB lift-out technique. The specimen structure is maintained for subsequent TEM analysis.

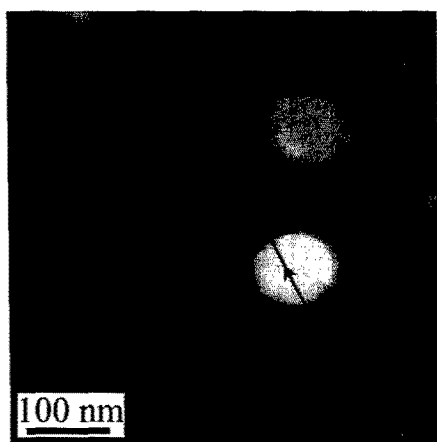


**Figure 5:** Bright-field HRTEM image of microtwins in a  $\beta$ -SiC nanoparticle.

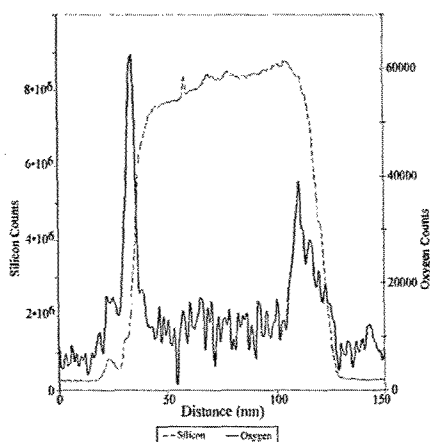
important to maintain the film-substrate interface and internal porosity of the structure, as these factors influence the properties of the film. It must be noted that the use of traditional TEM specimen preparation methods would require these pores filled with epoxy to stabilize their structure. Here, the FIB provides a precise method that does not require such procedures, and provides a large intact electron transparent area for subsequent TEM analysis [12].

In addition to the characterization of nanoparticle films, individual nanoparticles produced by HPPD have been analyzed. Using the focused beam deposition stage of the HPPD apparatus, it is possible to deposit lines of nanoparticles directly onto TEM support films. The center of a line is densely populated by nanoparticles; however, if the specimen is examined away from the line, a sparse distribution of nanoparticles is found, allowing the examination of single nanoparticles. Atomic level analysis is then possible using HRTEM. An example of this characterization is illustrated in Figure 5, which is a bright-field HRTEM image of microtwins in a  $\beta$ -SiC nanoparticle. The changes in atomic stacking are evident across the twin boundaries. Here, the use of spherical aberration correction in the HRTEM provides direct imaging of defect structure without the need for extensive image reconstruction, and will allow for a more complete understanding of growth- and mechanically-induced defects in nanoscale materials.

Analysis of the identity of chemically distinct surface layers is possible using analytical TEM. Figure 6 is a scanning TEM (STEM) image which denotes the path of an electron energy loss spectrum (EELS) line scan across a Si nanoparticle. A spectrum was collected every 1 nm along the path. The Si and O signals are shown in Figure 7 as a function of distance for the line scan. The shape of the oxygen profile is expected for a nanoparticle composed of a Si core that has oxidized at the surface. At the edge of the particle, only the oxide layer is sampled by the electron beam, leading to a large O signal. Conversely, the diminished oxygen signal in the bulk of the particle is due to the interference of the bulk Si core, which effectively masks the oxide signature. As oxide layers are deleterious to some potential nanoscale applications, identifying the presence of certain chemical species in nanoparticles has great importance for the development of the HPPD process.



**Figure 6:** Annular dark-field STEM image designating the path of a line spectrum across a Si nanoparticle.



**Figure 7:** Electron energy loss spectra for the line scan shown in Figure 6. The oxygen signal indicates the presence of a surface oxide layer for the Si nanoparticle.

## CONCLUSIONS

This study has illustrated the ability to produce and characterize both nanoparticle films and individual nanoparticles. The HPPD system is capable of high-rate deposition of chemically diverse structures. The techniques described for sample preparation and analysis provide opportunities for understanding nanoparticle formation and structure, as well as facilitating feedback on the performance of the HPPD apparatus. This combination will lead to tailoring the HPPD system for the production of nanoparticle-based functional structures. Further structural and chemical analysis of nanostructures will provide information to investigate material properties at the nanoscale.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. R.W. Siegel. *Materials Science and Engineering* 1993;**A168**: 189.
2. H. Gleiter. *Progress in Materials Science* 1989;**33**: 223-315.
3. N.P. Rao, N. Tymiak, J. Blum, A. Neuman, H.J. Lee, S.L. Girshick, P.H. McMurry and J. Heberlein. *Journal of Aerosol Science* 1998;**29**: 707-720.
4. J. Blum, N. Tymiak, A. Neuman, Z. Wong, N.P. Rao, S.L. Girshick, W.W. Gerberich, P.H. McMurry and J.V.R. Heberlein. *Journal of Nanoparticle Research* 1999;**1**: 31.
5. F. DiFonzo, A. Gidwani, M.H. Fan, D. Neumann, D.I. Iordanoglou, J.V.R. Heberlein, P.H. McMurry, S.L. Girshick, N. Tymaik, W.W. Gerberich and N.P. Rao. *Applied Physics Letters* 2000;**77**: 910-912.
6. F.A. Stevie, C.B. Vartulo, L.A. Giannuzzi, T.L. Shofner, S.R. Brown, B. Rossie, F. Hillion, R.H. Mills, M. Antonell, R.B. Irwin and B.M. Purcell. *Surface and Interface Analysis* 2001;**31**: 345-351.
7. J.K. Lomness, L.A. Giannuzzi and M.D. Hampton. *Microscopy and Microanalysis* 2001;**7**: 418-423.
8. D.M. Longo, J.M. Howe and W.C. Johnson. *Ultramicroscopy* 1999;**80**: 69-84.
9. T. Yaguchi, H. Matsumoto, T. Kamino, T. Ishitani and R. Urao. *Microscopy and Microanalysis* 2001;**7**: 287-291.
10. K.C. Grabar, K.R. Brown, C.D. Keating, S.J. Stranick, S.-L. Tang and M.J. Natan. *Analytical Chemistry* 1997;**69**: 471-477.
11. D.B. Williams and C.B. Carter. *Transmission Electron Microscopy*, Plenum Press, New York (1996).
12. C.R. Perrey, C.B. Carter, P.G. Kotula and J.R. Michael. *Microscopy and Microanalysis* 2002;**8**: 1144CD.

# **Polymer-Based Nanostructured Materials**